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Group Separations by Anion-Exchange.

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ABSTRACT

The combined work of many authors has pointed out the suitability of anion exchange as a means of separating cations, first by complexing them with an appropriate complexing agent and then by treating the complex formed with anion exchange resin. This work was undertaken in an attempt to apply such a method to a large group of ions in order to break it down into smaller groups suitable for analysis.

The ions used in this study were the ions generally covered in a student qualitative analysis scheme with the exception that ions requiring strong acids to maintain solution were omitted. In all, sixteen ions were covered. Citrate ion in the form of ammonium citrate and citric acid was used as the complexing agent.

Equilibrium experiments were carried out at constant acid concentration with varying citrate concentrations and at constant citrate concentration with varying acid strength. Both types of experimentation were also applied to column work and good separations were obtained by varying the citrate concentrations. Separations obtained by merely varying the acid strength were generally unsatisfactory.

The sixteen ions were separated into four groups. Mercury, barium, strontium and calcium were eluted by 50

milliliters of 0.1 M citrate; silver, lead, cadmium, magnesium and manganese by 50 milliliters of 0.5 M citrate followed by 50 milliliters of 1 M citrate; cobalt, copper, aluminum, nickel and zinc were eluted by 50 milliliters of 1 M citric acid. Iron and chromium were found to be tenaciously absorbed under these conditions and had to be eluted with 130 milliliters of 0.5 M hydrochloric acid.

Each group obtained was further broken down where it was necessary for a specific test to be made for each ion. In some cases no further separations were necessary.

The separations were not completely clean, there being a slight overlap between groups I and II. Judicious discarding of ten milliliters of eluant between these gives two well separated groups with only a slight loss of material. Group II can also be broken down into two sub-groups in the same manner.

The efficiency of separation of the ions was obtained by application of spot test techniques. Suitable tests were applied to each ion, and by successive dilutions the minimum amount of the ion present in each five milliliter fraction was obtained. By plotting this concentration against the volume increment, elution curves were obtained.

CHAPTER I

INTRODUCTION

The first recorded reference to the phenomenon of ion-exchange is found in the works of Aristotle[1], who, noting that water near the sea was often low in salt content, suggested that the water was rendered potable by percolation through the soil. Over a hundred years ago Thompson[2] and Way[3] made a complete study of ion exchange taking place in soils. They found that exchange took place in equivalent amounts but that the tendency to exchange was not the same for all ions. Some ions were found to exchange much more rapidly than others. Following this work the development of ion-exchange was very slow. This was due largely to the limitations of the naturally occurring exchangers which were then available.

The development of synthetic ion-exchange polymers gave great impetus to the growth of ion-exchange as an analytical technique. The first synthetic exchanger was prepared in 1935 by Adams and Holmes.[4] They also proposed a number of possible uses for their product. Other improved synthetic exchangers followed closely, both cation and anion. At present there are a number of synthetic resins being

manufactured, a typical cation resin being a sulfonated polystyrene, while a typical anion exchanger resin is a quaternary amine polystyrene. The anion exchange resins have been found to be particularly useful because many metals are capable of existing in the form of various negatively charged complex species.

Many complexing agents have been used in anion exchange separation of metals. The most widely studied has been the chloride ion, either in hydrochloric acid solutions or in a salt such as lithium chloride. Kraus and Moore[5] found that a partial separation of zirconium and hafnium could be obtained in a hydrochloric acid-hydrofluoric acid mixture. The same authors made a detailed study of anion exchange behavior of other metals in HCl and achieved many separations. For example, ferric iron was found to absorb at concentrations of 3 M or greater in HCl. This led the way to the investigation of the transition metals in HCl solution. Cobalt was found to have a maximum absorption at all concentrations.[7] When a mixture of the transition metals manganese through zinc[8] was investigated, a separation was obtained by successively decreasing the acid concentration starting with concentrated HCl. Nickel was eluted in 12 M HCl, manganese in 6 M, cobalt in 4 M, copper in 2.5 M, iron in 0.5 M and zinc in 0.005 M. This procedure has been adapted to the determination of nickel, manganese, cobalt and iron in alloys by Hague and coworkers.[9]

Separations that were unobtainable by the use of

hydrochloric acid alone could sometimes be achieved by the use of mixtures. Kallmon, Steele and Chu[10] separated zinc and cadmium utilizing 0.12 M HCl with 100 grams of sodium chloride per liter added. The zinc was removed by 2 M NaOH containing 20 grams of sodium chloride per liter and cadmium was removed by 1 M nitric acid. Kraus and Moore[11] separated zirconium and niobium by using a mixture of hydrochloric acid and hydrofluoric acid.

Work was then begun by Kraus and co-workers[12] to determine if solutions of a salt like lithium chloride would have the same effect as a hydrochloric acid solution of the same concentration. Since LiCl and HCl have activity coefficients in aqueous solutions which are similar, they expected to find the same absorption behavior. However, they found considerably greater absorption from the salt solution than from the acid solution, the distribution coefficients differing by a factor of approximately one hundred. Lithium chloride was then used by Herber and Irvine[13] to study the behavior of nickel since nickel had previously been found to be unabsorbed at all acid concentration. No absorption of nickel was noted from solutions as high as 8 M in LiCl.

Other complexing agents have also been investigated. Herber and Irvine[14] studied cobalt, copper, nickel and gallium with hydrobromic acid and found that absorption was similar to those found in hydrochloric acid with the exception of gallium, which was absorbed to a much lesser degree from hydrobromic

acid. Kraus and Nelson[15] separated iron from aluminum in sulfate solution, lead from bismuth[16] in nitrate solution and the alkaline earths[17] in citrate solution. Nelson[18] studied the anion exchange behavior of the alkali metals in ethylenediaminetetraacetic acid solution. Teicher and Gordon[19] separated iron from aluminum by absorbing the iron as the $Fe(CNS)_6^{=}$ iron. Smith and Reynolds[20] separated Sn (IV), Sb (V), and Te (IV) by using oxalic acid and sulfuric acid. Blasuis and Newger[21] separated gallium and iron as the oxalate complexes.

In the standard scheme of qualitative analysis, group separations are carried out by using differences in solubility of the various compounds under different sets of conditions. These separations are not always as good as one might desire. The precipitate of one group will almost invariably be contaminated by ions of the subsequent groups due to such phenomena as coprecipitation and occlusion. This work was undertaken to investigate the possibility of obtaining group separations by means of an anion exchange column. As has been shown, previous work indicated that a considerable number of separations can be carried out by use of anion exchange. No one author has attempted to deal with a large number of elements, but the underlying principles would be the same.

The first problem was to choose a suitable complexing agent. As has been noted, chloride has been widely used. It suffered from the disadvantage that there are insoluble chlorides. No other complexing agent used before had the wide

range of chloride. Oxalate was considered, but it also produced too many insoluble compounds. Work by Kraus and Nelson previously cited indicated the use of citrate ion as a complexing agent for the alkaline earths. Survey of the literature has shown ample evidence for the existence of citrate complexes of almost all the ions under study. Evidence has also been presented to show that these ions can exist in different negatively charged forms. This makes them particularly adaptable to anion exchange separations.

Dei[22] reported the existence of a citrate complex of silver having the composition Ag_3 $(Cit)_2$. Patnaik and Pani[23] stated that lead forms the following complexes: An insoluble species with the composition Pb H_2 Cit, and the following soluble species with increasing pH - $[Pb\ (H_2O)\ H\ Cit]^-$, $[Pb(H_2O)\ Cit]^=$, $[Pb(OH)\ Cit]^{\equiv}$, and $[Pb(Cit)_2]^{\equiv}$. Rabindra, Patnaik and Pani[24,25] demonstrated the existence of nickel complexes of the composition Ni H_2 Cit, $[Ni(H_2O)H\ Cit]^-$, $[Ni\ (OH)\ H\ Cit]^=$, $[Ni\ (H_2O)\ Cit]^=$. Cadmium complexes of the type $[Cd\ Cit]^-$ and $[Cd\ H\ Cit]^0$ and zinc complexes of $[Zn\ Cit]^-$ and $[Zn\ (OH)\ Cit]^=$ were shown to exist by Meites.[26] Bobbtelsky and Jordan[27] studied the citrate complexes of copper and nickel. They stated that the complexes seemed to be formed in a 1:1 ratio. They also stated that divalent metals would not form negative complexes with citric acid but tervalent metals would. This view is borne out by the work of Talaeva and Tikhonov[28] which demonstrated the existence of

$[Cu\ H_2\ Cit]^+$ in citric acid. If the pH is raised, other complexes of copper can be formed and these will be negatively charged. The work of Hamm, Shull and Grant[29] also bears out the contention that tervalent metals will form negative complexes in citric acid. These authors show the existence of at least two negative species of iron complexes with citric acid, $[Fe\ (OH)\ Cit]^-$ and $[Fe\ (OH)_2\ Cit]^=$. On the other hand, aluminum, also a tervalent metal, is shown to exist as the $[Al\ H_2\ Cit]^+$ ion in citric acid solutions.[30] The alkaline earths are said to form citrate complexes with a charge of minus one,[31] although one author[32] also postulated the existence of these ions: $[CaH_2Cit]^+$ and $[Ca\ H\ Cit]^0$. No information on the citrate complexes of chromium, manganese and mercury could be found in the literature.

With so many different forms of citrate complexes said to exist, citrate seemed a good choice as the complexing anion. The elements used in this study were the ones found on the standard qualitative scheme as taught at the sophomore level in chemistry. Some ions were omitted, those being the ones requiring strong acids to keep them in solution. These ions are Sb (III), Sn (II) and Sn (IV), Bi (III), Hg_2 (I), and As (III). In addition, only the Fe (III) was used due to the difficulty with air oxidation of Fe (II). The ions covered in this study were monovalent silver, divalent lead, calcium, barium, strontium, magnesium, copper, cobalt, nickel, cadmium, mercury and zinc, and tervalent aluminum, chromium

and iron.

CHAPTER II

EXPERIMENTAL

Reagents and Analytical Procedures

A 2 M solution of citric acid was prepared by dissolving 420 grams of reagent grade citric acid monohydrate in sufficient water to make one liter of solution. This solution was used for smaller concentrations by making the appropriate dilutions. A one molar solution of ammonium citrate was made by mixing equal quantities of the 2 M citric acid and 6 M ammonium hydroxide. Smaller concentrations of the ammonium citrate were made by diluting the 1 M solution.

A stock solution of aluminum was prepared by dissolving 37 grams of the nonohydrate of aluminum nitrate, reagent grade, in one liter of solution. This solution was standardized by precipitating the aluminum as the 8-hydroxyquinolate and weighing. It was found to contain 2.92 milligrams of aluminum per milliliter.

Approximately 26 grams of reagent grade barium nitrate were dissolved in one liter of solution. The solution was standardized by precipitating as the sulfate and weighing. The solution was found to contain 11.14 milligrams of barium per milliliter.

Metallic cadmium was used to prepare the stock solution. Approximately 10.8 grams of the metal were dissolved in nitric acid. After several evaporations to dryness, the excess nitric acid was removed and the solution was made up to one liter by addition of distilled water. The cadmium content of the solution was obtained by precipitating as the ammonium phosphate, igniting to the pyrophosphate and weighing. The solution was found to contain 10.84 milligrams of cadmium per milliliter.

Approximately 16.4 grams of reagent grade calcium nitrate were dissolved in sufficient water to make one liter of solution. The solution was standardized by precipitation as the oxalate and titration of the calcium oxalate in acid solution with a standard solution of potassium permanganate. The solution was found to contain 4.4 milligrams of calcium per milliliter.

A solution of chromium nitrate was prepared by dissolving 40 grams of $Cr(NO_3)_3.9H_2O$ in sufficient water to make up one liter of solution. The solution was analyzed for its chromium content by oxidizing the chromic ion to chromate with hydrogen peroxide, adding potassium iodide and titrating the iodine produced with standard thiosulfate. The solution contained 4.65 milligrams of chromium per milliliter.

Approximately 29 grams of the reagent grade hexahydrate of cobaltous nitrate were dissolved in one liter of solution. Cobalt (II) was oxidized to cobalt (III) with sodium perborate

and the cobalt (III) was treated with potassium iodide in sulfuric acid solution. The iodine produced was titrated with standard sodium thiosulfate solution. There were 6.68 milligrams of cobalt in each milliliter of solution.

A sufficient quantity of analytical grade cupric sulfate trihydrate was dissolved in water to make a solution which was approximately 0.1 M. This required about 241 grams of the cupric salt. The exact concentration of cupric ions in the solution was determined by the addition of potassium iodide and titration of the resulting iodide with standard sodium thiosulfate. The solution was found to contain 8.91 milligrams of copper per milliliter.

Thirty-five grams of the hexahydrate of ferric nitrate were dissolved in sufficient water to make one liter of solution. This solution was approximately 0.1 M. The solution was not used for some time and upon standing extensive hydrolysis took place with the subsequent precipitation of ferric hydroxide. For this reason, when the solution was standardized, it was found to be considerably lower in concentration than originally. It was therefore restandardized upon each using, but no further appreciable change took place. The standardization was carried out by the addition of potassium iodide and the titration of the iodine produced by standard sodium thiosulfate. The solution was found to contain 1.35 milligrams of iron per milliliter.

A standard solution of lead was prepared by dissolving

17 grams of lead nitrate in sufficient water to make one liter of solution. The solution was standardized by precipitating the lead as lead chromate and weighing. The solution was found to contain 11.3 milligrams of lead per milliliter.

A stock solution containing 17.27 milligrams of manganese per milliliter was prepared by dilution of an approximately fifty per cent reagent grade manganous nitrate solution. The solution was standardized by precipitating as the ammonium phosphate, igniting to the pyrophosphate and weighing. In practice, this solution was diluted with an equal amount of water to keep the manganese concentration approximately equal to the other ions under consideration.

Approximately 16.7 grams of the hemihydrate of mercuric nitrate were dissolved in sufficient water to make one liter of solution. Ten milliliters of nitric acid were added to facilitate solution. The mercury content of this solution was determined by precipitating as the sulfide and weighing. The solution was found to contain 10.23 milligrams of mercury per milliliter.

Approximately 50 grams of the hexahydrate of nickelous nitrate were dissolved in sufficient water to make one liter of solution. The solution was standardized by precipitating the nickel with dimethylglyoxime. The solution contained 10.43 milligrams of nickel per milliliter.

A stock solution of silver nitrate was prepared by dissolving about 17 grams of silver nitrate in sufficient

water to make one liter of solution. The silver content of this solution was determined by precipitating with sodium chloride and weighing. The solution contained 10.48 milligrams of silver per milliliter. This solution was stored in a brown bottle and kept in the dark as much as possible.

A solution of strontium nitrate was prepared by dissolving about 20 grams in sufficient water to make a liter of solution. The solution was standardized by precipitating the strontium as the oxalate, dissolving the precipitate in sulfuric acid and titrating the oxalate with standard potassium permanganate. The solution contained 8.84 milligrams of strontium per milliliter.

Approximately 30 grams of the hexahydrate of zinc nitrate were dissolved in sufficient water to make one liter of solution. The solution was analyzed for its zinc content by precipitating zinc as the phosphate and weighing. The zinc content was found to be 6.93 milligrams per milliliter.

The anion-exchange resin used in this work was Dowex-2, a strong base, quaternary amine polystyrene resin. The manufacturer's specification on this resin were as follows: capacity, approximately three milliequivalents per dry gram; moisture content, 40-45 per cent; porosity, medium, particle size, 100-200 mesh. The only refinement necessary for this resin to be used in column work was the removal of very fine particles. This was done by stirring the resin in a beaker with water, allowing it to settle and pouring off the fine

particles which remain suspended. After repeating this several times, the major part of the fine particles are removed and the resin is suitable for use.

The resin as it comes from the manufacturer is in the chloride form. For the purpose of this study it was necessary to convert it to the citrate form. This was accomplished by packing a large column with the resin and washing it at the rate of 1-2 milliliters per minute with a 0.1 M solution of ammonium citrate. When no test for chloride could be obtained in the effluent, the resin was considered to be in the citrate form. For a column 100 centimeters long and 4.5 centimeters in diameter, the amount of citrate solution required was approximately eleven liters. After conversion the resin was transferred to a large, wide mouth, glass stoppered bottle where it was kept under a solution of citrate ion. When resin was needed, it was removed, and the excess citrate was washed out with distilled water. One batch of resin conditioned in this manner was used throughout this study.

Equilibrium Studies

In column work involving anion exchange there are two equilibria which must be considered. There is an equilibrium existing between the undissociated complex and the metal and complexing ions. For a complexing agent bearing a single negative charge this might be represented by a general equation of the type $M^{+x} + nY^{-} \rightleftharpoons MY_n^{-(n-x)}$. In the case

of citrate ion, the situation is somewhat more complicated. Depending on the pH, there may be three different anions involving citrate; the citrate ion itself with a minus three charge, the monohydrogen citrate ion with a minus two charge and the dihydrogen citrate ion with a minus one charge. In addition, when complexing with a metal, the hydrogen of the hydroxyl group may be involved as well as the hydrogens from the three carboxyl groups. For this reason, no simple general formula as the one above can be written for the reaction between a metal ion and citric acid or ammonium citrate. The basic principle involved is still the same. There will be an equilibrium involved between the undissociated complex and the metallic and citrate ions. This equilibrium can be changed by a change in concentration of either the metal or citrate.

The second equilibrium which must be considered is that existing between the absorbed complex and the unabsorbed complex. To illustrate this, an equation can be written of the type

$$(n-x)\ RY + MY_n^{-(n-x)} \rightleftharpoons R_{(n-x)}MY_n + (n-x)\ Y^-$$

In this equation, R represents the monopositive functional group of the resin, Y represents a mononegative complexing agent, M is the metal of charge x and n is the number of ions of the complexing agent present in the complex. This equation is good only for the case where the complexing agent carries a minus one charge. If the functional group of the

resin is monopositive, conditioning with an excess of citrate ion would seem to produce R_3X where $\underline{X}$ represents the minus three citrate ion. If the resin is considered to be wholly in this condition, then the reaction taking place on the resin where the $\underline{X}$ is replaced by the complex must depend upon the charge on the complex. However, there must also be considered the possibility that some of the resin may be in the form R_2HX and RH_2X depending on the amount of hydrolysis. Also, in the presence of a large amount of citrate ion there is no assurance that only the R_3X form of the resin might be formed. There is also the possibility that one molecule of the resin might only satisfy part of the coordination possibilities of the citrate ion. This might best be represented in the following equation:

$$RCl + (NH_4)_3 X \longrightarrow RX(NH_4)_2 \longrightarrow R_2X(NH_4) \longrightarrow R_3X$$

This equation represents the possible steps that could take place when the resin in the chloride form is conditioned with ammonium citrate. For one citrate ion to be completely complexed with the resin requires that three positive groups be in proper position to satisfy the spatial charge requirements of the citrate ion. At the same time, there is competition among the citrate ions for the available sites. If some of the resin is in the form $RX(NH_4)_2$ or $R_2X(NH_4)$, then absorption of the metal ions or the complex species might be altered in some fashion.

The above discussion points out the inadvisability of

attempting to write one single equation which would show the mode of absorption of the complex species with the resin. One thing is certain--there is an equilibrium involved in the absorption process. This equilibrium will depend upon the condition of the resin and the absorption characteristics of the complex species. If the resin is conditioned in the same fashion and if the complex is formed in the same manner, the absorption characteristics should be the same. Changing the concentrations of the complexing ion will change the nature of the complex and will therefore alter the absorption characteristics.

The equilibrium distribution of a metal between the absorbed (resin) phase and the unabsorbed (liquid) phase is conveniently represented by a distribution coefficient, which is defined as:

$$K_d = \frac{\text{amount of metal in resin}}{\text{amount of metal in solution}} \times \frac{\text{total volume of solution}}{\text{mass of resin}}$$

This distribution coefficient is very useful in predicting the absorption behavior of a particular complex species. It is particularly useful where a large number of ions is under investigation. Distribution coefficients which are similar indicate that the ions will behave alike on the column, whereas separations can be obtained only where the distribution coefficients are different.

Distribution coefficients can be determined from column studies but the easiest method is a batch process in which

measured amounts of the resin and the ion under study are allowed to come to equilibrium and the relative amounts in each phase determined. Two equilibrium studies were made in this fashion, one in which a fixed concentration of citrate ion was used and the hydrogen ion concentration varied by the addition of perchloric acid, and the other in which varying concentrations of citrate ion were used.

In both cases the following procedures were used. The resin was removed from the stock bottle and filtered under suction. The excess citrate was removed by washing with distilled water until the effluent gave no further test for citrate. The resin was pressed dry and then allowed to air dry under suction for one half hour. The resin was then dry enough to handle easily and was found to have a fairly uniform water content. A number of determinations of the water content of a batch of resin treated in this fashion were made and the water content was found to vary from 38 to 40 per cent. Since the equilibrium studies were intended merely as a guide in column studies, such accuracy was deemed sufficient. Therefore, in all batch experiments, exactly three grams of resin prepared in this manner were used. The resin was placed in a 250-milliliter flask and five milliliters of the stock solutions were added. Following this step, the procedure was different depending on which equilibrium study was being carried out. In the study where the acid concentration was being varied, exactly five milliliters

of 0.1 M ammonium citrate were added and sufficient perchloric acid added to make the solution a given strength in acid. The total volume of the solution was kept at fifteen milliliters. The acid strengths used in this study were 0.025 M, 0.05 M, 0.1 M, 0.15 M, 0.2 M, 0.25 M and 0.3 M. Every ion was not run at all concentrations. The flask was then stoppered, placed on an automatic shaker and shaken for twenty-four hours. After being removed from the shaker, the contents of the flask were filtered, and the concentration of the given ion in the solution determined by the same method used for standardization. The concentration of the ion on the resin was obtained by difference and the distribution coefficients calculated.

The distribution coefficients for the experiments in which pH was kept constant and the citrate ion concentration varied were determined in the same fashion. Each ion was placed in a flask with three grams of resin and five milliliters of 0.1 M, 0.5 M and 1 M ammonium citrate. After being shaken for twenty-four hours, the mixtures were filtered and the concentration of the ion determined by the same method used for standardization. An appreciable number of elements were found to absorb strongly at all concentrations, so an additional equilibrium study was made in 1 M citric acid.

Column Studies

A simple column was prepared by drawing out the end of

ten millimeter glass tubing just enough to enable a glass wool plug to support the weight of the column of resin. A small piece of rubber tubing was attached at the bottom, and to this was attached a glass tip. The flow through the column was controlled by a screw clamp on this rubber tubing. A reservoir of approximately one hundred milliliters capacity was arranged by connecting an ordinary, short stem funnel to the column by means of a short piece of rubber tubing. This apparatus, while very simple in nature, served very well throughout this study. The resin bed was prepared as follows: the screw clamp was opened to allow maximum flow rate and the ammonium citrate suspension of the resin was poured in and allowed to settle while filtering. The column prepared in this manner was 26 centimeters long. A piece of glass wool was placed on top to prevent the resin from being disturbed while solutions were added to the column. When the resin bed was of the proper length and the resin apparently had settled completely, the column was washed with distilled water until all the excess citrate had been removed. The resin bed was not allowed to become dry, however, since this quite often would result in channeling.

Each ion in this study was placed on the column alone at first. This was in order to determine the approximate volume necessary for elution. The ions were then placed on the column in groups and finally the entire sixteen ions were placed on together. In order to ensure that the capacity of

the resin was not being exceeded, small amounts of the ions were used. In all cases, two drops of the stock solutions were placed directly on the column, followed by the eluting solutions. Elution was carried out by fifty milliliter portions of 0.1 M, 0.5 M and 1.0 M ammonium citrate and 1 M citric acid. Two ions were difficult to remove under these conditions and an additional 130 milliliters of 0.5 M hydrochloric acid was necessary to complete the removal of all the ions. The column was most efficient when operated at a flow rate of 1 to 1.5 milliliters per minute. The effluent was collected in five milliliter portions in test tubes and analyzed qualitatively for each particular ion. In most cases standard qualitative tests were applicable. However, in the case of three ions, special steps had to be taken. For example, the lake test for magnesium using the S and O reagent (p-nitrobenzeneazoresorcinol) was very slow in forming. This was due to the decreasing of the hydroxide ion concentration by the common ion effect of the large amount of ammonium ions present in the solution. This could be corrected by heating the solution with sodium hydroxide in order to remove as much of the ammonium ion as possible as ammonia gas. Also, neither the benzidine test nor the bismuthate test for manganese would work in 1 M ammonium citrate. In this case manganous hydroxide was precipitated by sodium hydroxide, the precipitate dissolved in nitric acid and the bismuthate test run. Finally, no qualitative test for aluminum could be carried out either

in citrate or citric acid solution. This necessitated taking the five milliliter portions to dryness, ashing in the muffle furnace, dissolving the ash in 1 M nitric acid and determining aluminum by the fluorescent test with morin.

After group separations were obtained, the efficiency of separation had to be determined. In dealing with such small amounts of materials the ordinary means of quantitative analysis were clearly out of the question, so other methods had to be devised. It was decided to apply spot test techniques to get an approximate concentration of the ion in each five milliliter portion. There are a number of very sensitive spot test reactions for each of the metals. The analyses were carried out as follows: The sensitivity of each spot test was determined for the particular conditions under which it was being applied by taking a known amount of the ion and successively diluting it until no test could be obtained. The same technique was applied to each five milliliter portion of the effluent. In this manner, the minimum concentration of the ion in each portion was determined. This method fixes the concentration as being not less than the amount calculated for the last dilution in which the test appeared and possibly more, up to the next dilution. The concentration of each ion was plotted against the effluent volume and in this manner, elution curves were obtained.

The spot tests used were all taken from the book by Feigl[33]. Aluminum was determined by the fluorescence

produced with morin in ultraviolet light. Barium and strontium were determined by precipitation with sodium rhodizonate, cadmium by precipitation as $CdI_4^=$ with ferrous α, α dipyridyl, Ca by precipitation with dihydroxytartaric osazone, cobalt by the blue color produced with thiocyanate ion and acetone, copper with dithiooxamide, nickel by precipitation with dimethylglyoxime, iron by the red color produced with thiocyanate ion, magnesium by the blue lake produced by p-nitrobenzeneazoresorcinol (S and O reagent), manganese by the oxidation of benzidine acetate to form a blue color, mercury by dithizone, lead by sodium rhodizonate, silver by dithizone, chromium by oxidation to chromate and the subsequent oxidation of benzidine to a blue color by the chromate and zinc by the induced precipitation of copper tetrathiocyanatomercurate (II).

CHAPTER III

RESULTS

Equilibrium Studies

The results of the equilibrium studies in which the hydrogen concentration was changed while the citrate concentration was kept constant are shown in Table I. All elements are listed with the exception of silver and lead. These could not be considered at this citrate concentration because they both form insoluble citrate compounds.

At acid concentrations of 0.025 M and 0.05 M copper, iron, chromium, aluminum, and zinc show complete absorption. No test for any of these ions could be obtained in the solution. At an acid concentration of 0.1 M, all except zinc are still absorbed completely. Zinc is still absorbed strongly here, but its distribution coefficient is beginning to decrease. Copper ceases to be completely absorbed at 0.15 M acid as is the case for chromium, although they are both still strongly absorbed. Iron absorbs completely up to 0.25 M acid. An acid concentration of 0.3 M is necessary to bring the distribution coefficient of chromium and aluminum to a point where successful elution could take place.

Cobalt, mercury, cadmium and nickel, while not

completely absorbed at any acid concentration, show quite strong absorption up to 0.05 M acid. At 0.2 M acid concentration cobalt, cadmium, mercury, and nickel are absorbed to only a fractional amount of what they had been and at 0.25 M acid concentration desorption is well advanced.

Calcium, magnesium and strontium are moderately well absorbed at an acid concentration of 0.025 M while barium and manganese are poorly absorbed. The absorption of all three of these decreases as the acidity increases with the exception of strontium which shows a uniform behavior up to an acid concentration of 0.15 M.

The results of the equilibrium studies involving a varying citrate concentration are shown in Table II. Chromium and aluminum were completely absorbed in 0.1 and 0.5 M citrate solution, whereas aluminum was apparently completely absorbed in 1 M citrate and 1 M citric acid. Iron, copper, cobalt, cadmium, and zinc showed very strong absorption in 0.1 M citrate with the absorption dropping off rapidly as the citrate concentration increased. In 1 M citric acid, copper, cobalt and zinc were poorly absorbed, but iron reversed its downward trend and again was completely absorbed. The absorption of cadmium which was high in 0.1 M citrate was found to drop off sharply in 0.5 M citrate. Nickel was strongly absorbed in 0.1 M citrate, with its absorption dropping off in 0.5 M, but not as abruptly as cadmium. Manganese, mercury, calcium, strontium and magnesium show a fair degree of

absorption in 0.1 M citrate. The absorption of all these decreased rapidly with increasing concentration. Barium was found to be poorly absorbed in 0.1 M citrate with the absorption decreasing still further with increasing concentration.

No distribution coefficient could be obtained for silver and lead in 0.1 M citrate, since they both form insoluble species. In 0.5 M citrate they both show an apparent degree of absorption which may not be true absorption, but a partial precipitation of the insoluble salt within the resin.

A simple series of tests were run in which solutions of the various ions were added to three gram portions of the resin with no additional complexing agent being added. In all cases, some absorption was noted and for the tervalent and some of the divalent metals such as copper, cobalt, nickel and zinc, complete absorption was found.

Column Studies

The distribution coefficients obtained in both equilibrium studies gave promise for the column separation of the various ions. Consequently, studies were run in which the ions were put on the column with 0.1 M citrate and elution was attempted by using solutions of the appropriate acid concentrations. It was found that the ions appeared in the effluent in the approximate order expected, although there was a large amount of tailing. No clean separations of one group from another could be obtained. Consequertly, the other line of attack was considered, the variation of the citrate

concentration.

The ions were placed directly upon the column, with no additional complexing agent being added. Just before the column ran dry, fifty milliliters of 0.1 M citrate were added, followed by fifty milliliter portions of 0.5 M and 1 M citrate and 1 M citric acid. The first ion to appear in the effluent was mercury, which appeared at 10 milliliters, peaked at 15 milliliters, gradually decreased and was completely gone at 60 milliliters. Barium first appeared at 20, calcium at 25 and strontium at 40 milliliters. The volume increment with the maximum concentration of each ion can be obtained from Figures 1 through 8, in which concentration of each ion is plotted against volume of effluent. The second group of ions was obtained from the 0.5 M and 1 M portions of the effluent. In these solutions, the following ions were found, in order: silver, lead, cadmium, magnesium and manganese. This group began at 60 milliliters and was completed at 160 milliliters. The third group consisted of nickel, copper, cobalt, zinc and aluminum. The first ion appeared at the 180 milliliter portion and the last ion was completely removed at 225 milliliters.

Two ions were found to be still absorbed at all concentrations of citrate ion and citric acid. Iron and chromium were finally removed by the use of 0.5 M hydrochloric acid. Under these conditions both the iron and chromium colors can be detected on the column. Iron first appears at 270

milliliters and was completely removed at 310 milliliters. Chromium first appeared at 310 milliliters and was completely removed at 330 milliliters.

The elution curves obtained by the spot test technique previously described are found in Figures 1 through 8. It should be noted that nickel appears in two places in these curves, in the 1 M citrate and in the 1 M citric acid. This was repeatedly found, and was considered to be possibly two species of nickel or two different complexes in which the rate of equilibrium is very slow.

Although the principal purpose of this study was to obtain group separations by anion exchange, the groups that were produced were further broken down by other chemical means and each ion identified by an appropriate test. In some cases, part of the effluent could be discarded in the interest of cleaner separation. In this way a mixture of ions was taken, broken down into groups and each ion identified by an individual test, or if necessary the groups may be further subdivided and each ion obtained alone.

The analysis may be carried out as follows. The first fifteen milliliters of the 0.1 M ammonium citrate portion are discarded and the remainder concentrated by evaporation to 20 milliliters. A five milliliter portion of this solution is treated with stannous chloride, and if mercury is present the entire solution turns grey due to the reduction of mercury (II) to metallic mercury. This is removed by centrifugation.

The remaining solution is treated with 1 M potassium chromate in slightly acid solution. Barium precipitates under these conditions and can be centrifuged out. Strontium sulfate will precipitate in slightly acid solution. This is best accomplished by the use of ammonium sulfate. Some calcium may coprecipitate, but this will not interfere with the flame test for strontium. Calcium is finally identified by precipitation as the oxalate in slightly acid solution. The precipitate must be washed carefully to remove any possible strontium ions that may be left in the solution. Washing with water will accomplish this purpose. In the case of barium, strontium and calcium, flame test may be used as confirmatory tests.

The second group composed of effluent from the 0.5 M and 1 M ammonium citrate fractions is treated as follows. The first ten milliliters are discarded. The group can then be subdivided into two groups if a portion of the effluent is discarded. The elution curves for this group show that if the 100-110 milliliter portion is discarded, some small amount of cadmium, magnesium and manganese are lost. The amount lost is adequately compensated for by the added ease of handling this group. There will now be two sub-groups, one with three ions: lead, silver and cadmium, and another group with magnesium, manganese and some nickel. The first sub-group is treated as follows: Silver is precipitated from a warm solution as the chloride and centrifuged out. Lead can be

precipitated from the centrifugate as the chromate. The cadmium which remains can be identified as the yellow sulfide. The second sub-group is treated with excess sodium hydroxide and heated. After standing a few minutes, manganous, magnesium and nickel hydroxides will precipitate. This precipitate is dissolved in 1 M nitric acid and each ion is identified separately, magnesium by the blue lake with 3 and 0 reagent, manganese as purple permanganate produced by oxidation with sodium bismuthate and nickel as red nickel dimethylglyoxime, precipitated in ammoniacal solution by the addition of dimethylglyoxime.

The third group composed of effluent from 1 M citric acid fraction has to be handled somewhat differently due to the difficulty of testing for aluminum in this solution. The solution in the 180-235 milliliter range is collected and evaporated to dryness in a crucible on the hot plate. The crucible is then placed in a muffle furnace at about 600° and ashed. The ash is then dissolved in 1 M nitric acid. The temperature of ashing must not be allowed to rise too high since zinc may be lost by volatilization. The nitric acid solution containing copper, cobalt, nickel, zinc and aluminum can be tested directly for aluminum by the fluorescent test using morin. If the solution is then treated with sodium hydroxide, copper, cobalt and nickel hydroxides precipitate and can be centrifuged. The solution can be tested for zinc either by precipitation of cobalt or

copper tetrathiocyanatomercurate (II). The hydroxide precipitate is dissolved in concentrated hydrochloric acid and copper reduced by sulfite and precipitated as the white cuprous thiocyanate by the addition of ammonium thiocyanate. After the copper has been removed cobalt and nickel can be identified independently of each other, cobalt by the blue color produced with ammonium thiocyanate and acetone and nickel by the red precipitate of nickel dimethylglyoximate.

The last group composed of effluent from HCl fraction is very simple to handle. Iron is identified by the red color with thiocyanate ion and chromium can be identified by oxidation to chromate with sodium peroxide and the reaction of this chromate ion with benzidine acetate in acetic acid solution to produce a blue color.

CHAPTER IV

DISCUSSION

In general, the ease of removal of the various ions from the resin bear out what would have been expected from the equilibrium data. The distribution coefficients obtained in the study using varying acid strength strongly suggest possible separations utilizing eluting agents of different acid strengths. Perhaps better separations would have been obtained if a mixture of perchloric acid and ammonium citrate had been used rather than simple acid solutions.

The absorption on an ion-exchange resin will depend on the charge on the complex and the size of the ion. In a solution of higher citrate concentration, the charge on the complex should be larger than the charge on the complex in lesser citrate concentration. This of course holds true only when the element is capable of forming more than one species. For this reason, it would be expected that better absorption would occur at higher citrate concentrations. In practice the exact opposite behavior has been found for almost all elements studied. This behavior has also been noted and reported on by Kraus and Moore.[17] Apparently the size of the ion must play an important part here. As the size of the ion

increases, it becomes more difficult for the ion to penetrate into the interstitial spaces and approach the exchange site.

The absorption process is said to take place in three steps. The ion must diffuse through the resin to the exchange site, exchange must take place and the displaced anion must diffuse away. When absorption is found to be considerably smaller in more concentrated solutions, it must be that the first step of the exchange process is the limiting factor. Therefore, the size of the ion is very important.

The order of elution takes place in a manner which can be related to the approximate sizes of the uncomplexed ions. Barium, mercury, strontium, silver, lead and calcium are the largest ions. All of these except silver and lead are in the first group to be removed. Silver and lead are insoluble in 0.1 M citrate solution and precipitate upon the resin. Therefore they cannot be eluted until the citrate solution is sufficient to put them back in solution. Cadmium and manganese are the next in size. They are found in the second group along with silver, lead and magnesium. Magnesium is the only one here whose size differs markedly from the rest. This points out what has been said before. Size is not the only criterion. Cobalt, nickel, copper, zinc and aluminum are found together. Of these five, only aluminum is very different in size. Here the nature of the complex seems to be more important. Aluminum and copper are said to form complexes in citric acid which are positively charged. It is probable that

the other three ions do likewise. The final two elements to come off the column are iron and chromium which are also of approximately the same size.

As pointed out before, both silver and lead citrate are somewhat insoluble and tend to precipitate upon the resin. This would explain the anomalous behavior found for these two ions. In the equilibrium work, where there was a small, fixed amount of citrate ion, distribution coefficients were obtained which would seem to indicate that strong absorption was taking place. It is very likely that this was not true absorption of the complex, but to a large degree, simple precipitation upon the resin. In column work, both ions behaved as if they were not strongly absorbed. In this work, there was a large amount of citrate solution, sufficient to dissolve any precipitate which might have been formed.

In an earlier section, it has been noted that ions placed directly upon the washed resin are still found to absorb, some to a very great extent. This is best explained by assuming that the resin is not completely in the R_3X form as previously discussed, but rather that some part of the resin must be in such a form that some of the coordination centers of the citrate ion are still free. If this were not so, the phenomenon would involve absorption of a cation by an anion exchange resin.

One possible explanation has already been advanced. If the reaction during the conditioning of the resin takes

place in the following manner,

$$RCl + (NH_4)_3X \longrightarrow R(NH_4)_2X \longrightarrow R_2NH_4X \longrightarrow R_3X,$$

then a cation could be absorbed simply by displacing one or more of the ammonium ions associated with the resin. This has been noted. If a sample of resin is washed with water until no ammonium ions appear in the effluent and then treated with a solution of some metallic ion, additional ammonium ions are found to appear indicating that these ammonium ions have been held on the resin and are being displaced by the cation.

In order to determine whether the ions showing a low degree of absorption were really absorbed by ion exchange or whether some simple surface absorption was taking place, the columns were washed with large amounts of water to see if any of the ions could be removed. They were all found to cling strongly, indicating that an appreciable bending was taking place.

Nickel has been found to behave peculiarly. As previously stated, a small amount of nickel was found to appear in the second group while the bulk of the nickel appeared in the third group. Two possible explanations may be offered. The first is that there are two species of nickel present, the nickel (II) and the nickel (III). However, since both forms found give the test with dimethylglyoxime which is generally considered to react with divalent nickel only, this seems not to be the case. The other explanation is that

these are two different anionic complexes of nickel, in equilibrium. This equilibrium would necessarily be slow, since it would involve a solid-liquid transformation. In any case, the two forms of nickel pose no serious problems for the qualitative scheme.

Aluminum was also found to behave in a peculiar fashion. At all concentrations of citrate ion used, aluminum is complexed strongly and is absorbed completely. In 1 M citric acid aluminum is still complexed strongly enough to make standard qualitative tests inapplicable. The complex, however, is now a positively charged one, and aluminum is rapidly eluted from the column. In order to detect it, the citric acid must be destroyed. This is done by ashing in a muffle furnace. Care must be taken to keep the temperature under 800°C because zinc will distill at approximately 900°C.

The qualitative scheme as developed in this manner has some drawbacks. The time involved to make all the separations will run from four to five hours. Additional time will be required in the breaking down of the groups due to the special procedures necessary in testing for such elements as magnesium, manganese and chromium. Also, care must be taken to keep iron impurities out of all solutions and reagents, since small amounts of iron tend to collect at the top of the column.

On the other hand, some worthwhile separations have been made. Cadmium is separated from mercury, which has always been a source of trouble. Since cadmium is generally identified as

the yellow sulfide, only a very small amount of mercury is necessary to discolor the precipitate. In this procedure, mercury will be completely removed before the test for cadmium is made. The alkaline earths are already broken down into two sub-groups, magnesium in one and calcium, strontium and barium in the other. Iron and chromium have been completely removed from aluminum. In the standard scheme of qualitative analysis they are a constant source of error in testing for aluminum.

As the elution curves show, there is only a small amount of overlap between groups I and II. If a ten milliliter fraction is discarded here, less than twenty micrograms of mercury and twenty micrograms of silver will be lost. If group II is broken down into two sub-groups by discarding the 100-110 milliliter fraction, about 250 micrograms of cadmium, 20 micrograms of lead, 170 micrograms of magnesium will be lost. This represents 1.9 per cent of the mercury, 1.9 per cent of the silver, 1.8 per cent of the lead, 15 per cent of the magnesium and 23 per cent of the cadmium. The last two figures represent appreciable amounts, but quite sufficient amounts of the two ions are left in solution to make a positive identification.

In the group which is eluted with citric acid, no ion appears until the citric acid breakthrough. Kraus and Moore[17] stated that the citrate form of the resin acts as a base and absorbs the citric acid. When the citric acid appears in the

effluent, elution generally begins. In the case of some of the ions, it may be delayed for 5-10 milliliters. In any case, this affords an excellent means for checking the progress of the elution. If the pH of the effluent is tested continuously there will be an abrupt drop from six to about one at the acid breakthrough. At this point the effluent is collected for analysis.

CHAPTER V

SUMMARY

Work by a number of authors which has been cited in the literature shows that a great many separations of metallic ions could be made by anion exchange, utilizing various complexing agents. This work was undertaken to see if the technique could be applied to a large number of ions by separating them into groups suitable for further analysis. After a careful study of the complexing agents available, citrate ion in the form of ammonium citrate was chosen. Equilibrium studies were carried out to see if changes in citrate concentration or changes in acid concentration would be most effective. The former procedure was found to be better and was then applied to column studies.

Sixteen ions were investigated, these being the ions normally found in a general qualitative scheme with the exception of those requiring strong acid to maintain solution. The ions were broken down into groups by using fifty milliliter portions of 0.1 M, 0.5 M and 1 M citrate solution and 1 M citric acid solution. Elution of the most difficult ions was carried out by 130 milliliters of 0.5 M hydrochloric acid. Four groups were obtained. Mercury, calcium, barium

and strontium were eluted by 0.1 M citrate; silver, lead, cadmium, magnesium and manganese by 0.5 M and 1 M citrate; copper, cobalt, nickel, zinc and aluminum by 1 M citric acid and finally iron and chromium by 0.5 M hydrochloric acid. The groups obtained could be broken down further by chemical means and each ion identified. By judicious discarding of certain portions of the effluent, the small amounts of overlap between groups I and II could be avoided. Also, discarding of a portion of the effluent in group II gives rise to two sub-groups, each one easily handled.

Elution curves for the small amounts of material used in this study were determined by applying the most sensitive spot tests available and carrying out a series of successive dilutions until no further test could be obtained. In this way, a semi-quantitative measure of the efficiency of separation was obtained.

TABLE I

DISTRIBUTION COEFFICIENTS IN 0.1 M CITRATE WITH VARYING ACID STRENGTH

Ion	Concentration of Acid						
	0.025M	0.05M	0.1M	0.15M	0.2M	0.25M	0.3M
Ba	1.4	0.37	1	1.36			
Mn	3.9	2.9	1.6	0.88	0.3	0.2	
Sr	6.5	5.9	5.2	5.5			
Mg	10.3	8.4	2.0	0.2			
Ca	12.9	11.3	6.2	5.2			
Ni	69	32.5	12.4	5.9	2.8	1.2	
Cd	79.4	45	17.7	11.0	4.5	0.1	
Hg	102	85.6	41	21.0	2.3	0.8	0
Co	242	60.4	13.3	7.5	3.8	2.2	
Fe	*	*	*	*	*	*	
Cr	*	*	*	203	43.4	25.1	9.4
Al	*	*	*	*	24	13.0	4.1
Zn	*	*	56	13.3			
Cu	*	*	*	58.9	25.2	5.1	

*Absorption apparently complete

TABLE II

DISTRIBUTION COEFFICIENTS IN AMMONIUM CITRATE AND CITRIC ACID SOLUTIONS

Ion	0.1M Citrate	0.5M Citrate	1M Citrate	1M Citric Acid
Ba	1	0.5	0.4	0.3
Sr	3.5	0.7	1.0	1.1
Ca	3.7	0.92	0.58	0.25
Hg	3.9	1.6	0.90	0.3
Mg	4.6	21	1.2	.13
Mn	5.5	3.5	1.3	0
Cd	50.5	2.4	1.1	*
Pb	Insoluble	3.52	2.9	1.4
Ag	Insoluble	6.9	5	0.4
Ni	20.9	5.35	2.4	0.96
Cu	106	8.3	4.5	24
Co	119	7	2.25	0.37
Zn	117	12.3	4.5	24
Fe	49	22.6	14.3	*
Cr	*	*	20.9	7.7
Al	*	*	*	*

*Absorption apparently complete

TABLE III

EFFICIENCY OF SEPARATION

Ion	Spot Test Used	Sensitivity[1]	Amount Put on Column[2]	Amount Recovered[3]	Per Cent Recovery[4]
Al	Fluorescence with morin	0.2	438	406	92.7
Ba	Sodium rhodizonate	.25	1112	1075	96.7
Cd	Ferrous α, α-diryridyl	.36	1084	1080	99.6
Ca	Diphydroxytartaric osazone	.08	1110	1046	94.2
Cr	Benzidine	.25	465	441	94.9
Co	Potassium thiocyanate-acetone	.3	668	660	98.8
Cu	Dithiooxamide	.2	891	890	99.9
Fe	Thiocyanate	.25	672	672	100
Pb	Sodium rhodizonate	.1	1130	1104	97.7
Mg	S and O	1.7	476	446	93.7
Mn	Permanganate	.1	864	780	90
Ag	Dithizone	.25	1024	965	94
Ni	Dimethylglyoxime	.75	992	912	92
Hg	Dithizone	.05	1048	1040	99
Sr	Sodium rhodizonate	3.9	884	860	97.3
Zn	Induced precipitation of Co $Hg(CNS)_4$	3	1041	960	92

[1] in micrograms [2] in micrograms [3] minimum [4] minimum

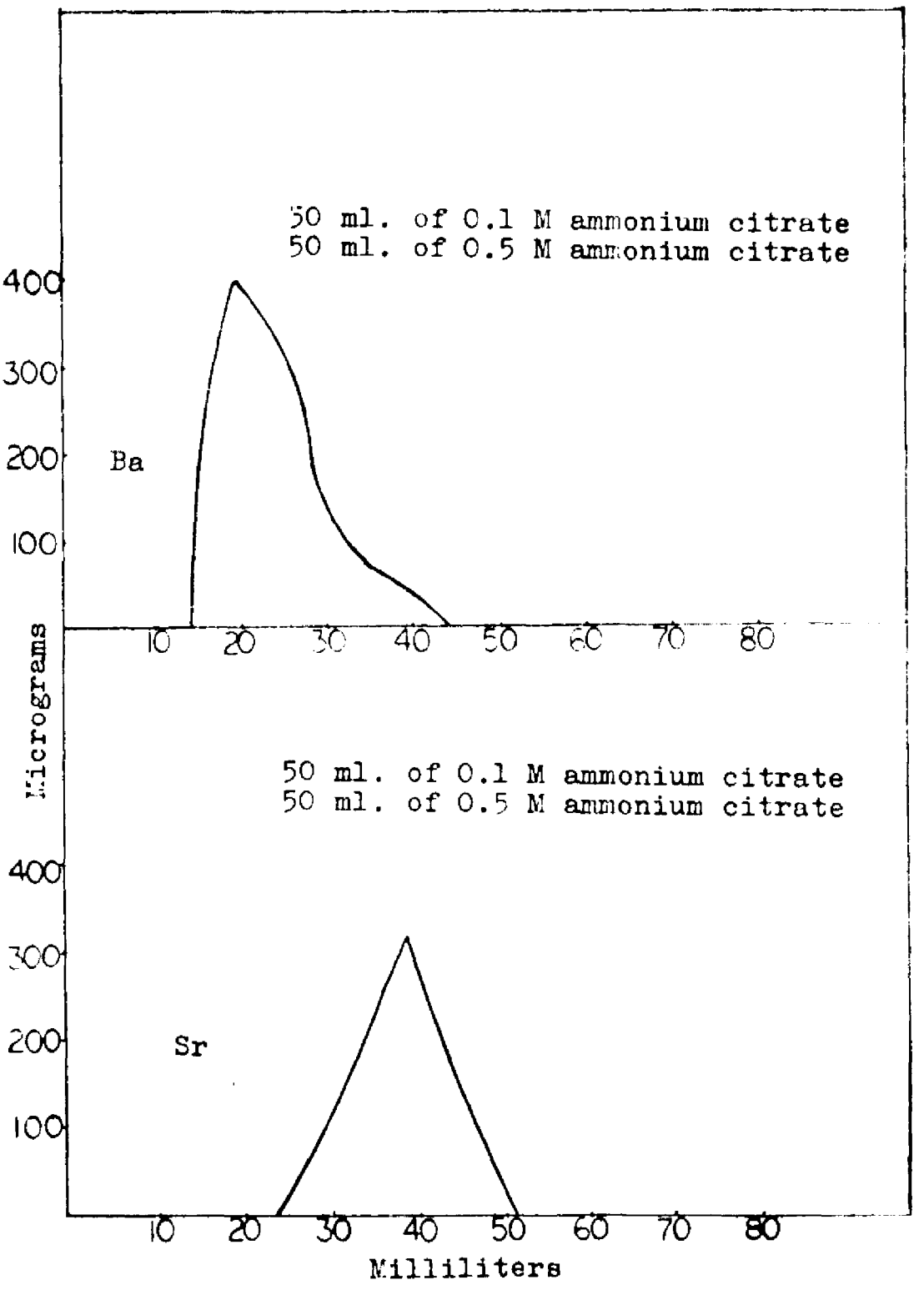

FIGURE 1

ELUTION CURVES FOR STRONTIUM AND BARIUM

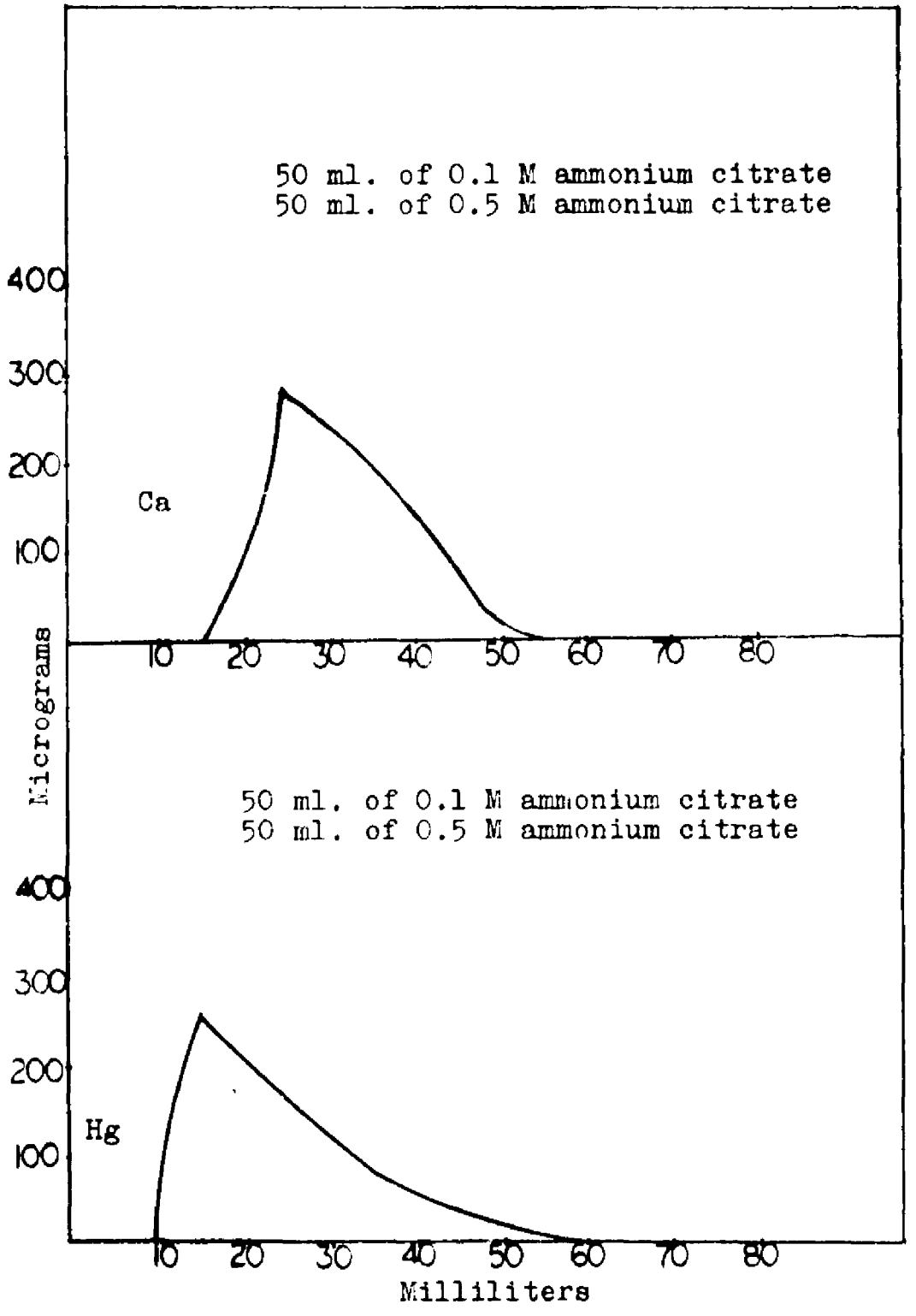

FIGURE 2

ELUTION CURVES FOR MERCURY AND CALCIUM

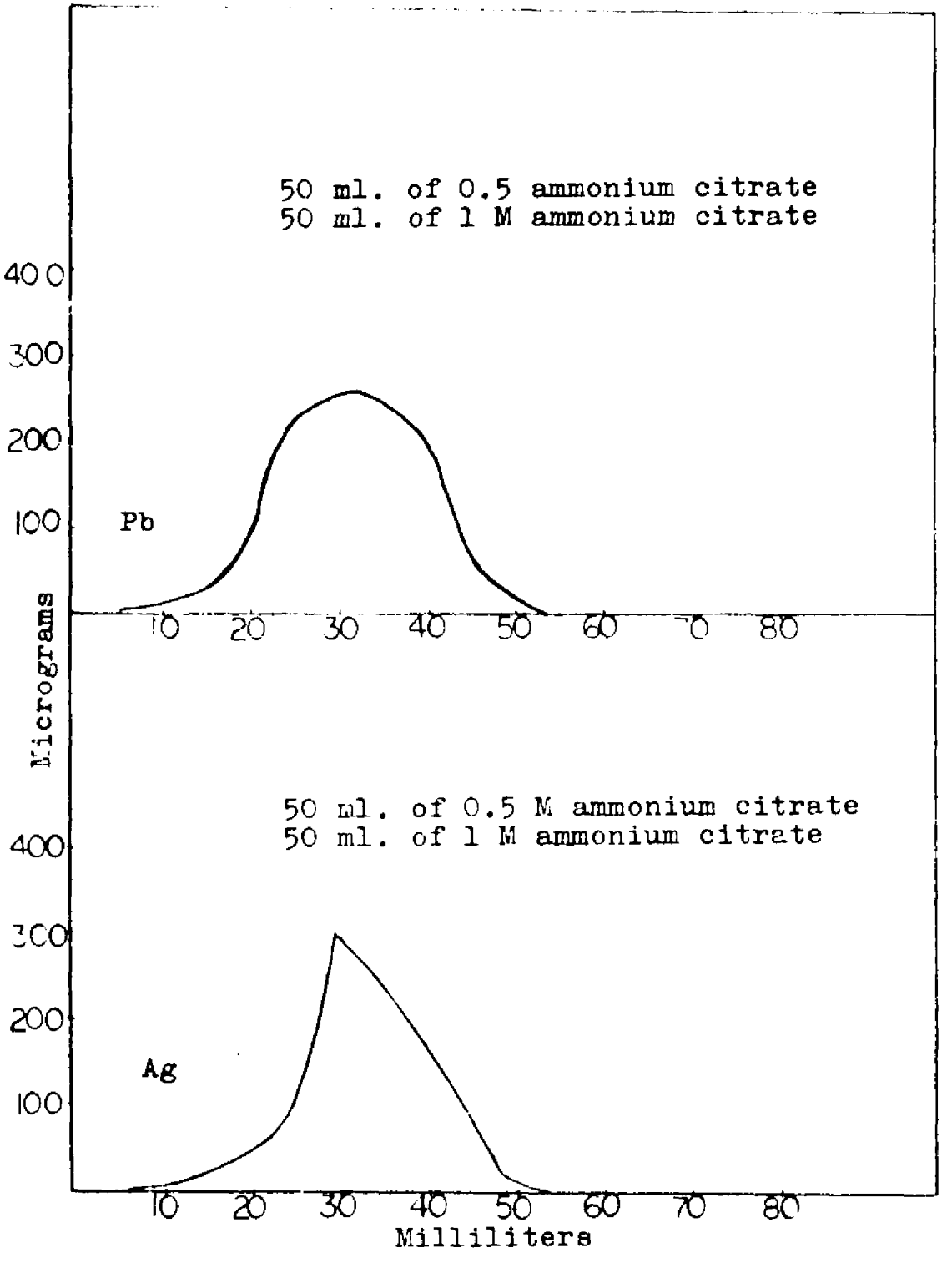

FIGURE 3

ELUTION CURVES FOR SILVER AND LEAD

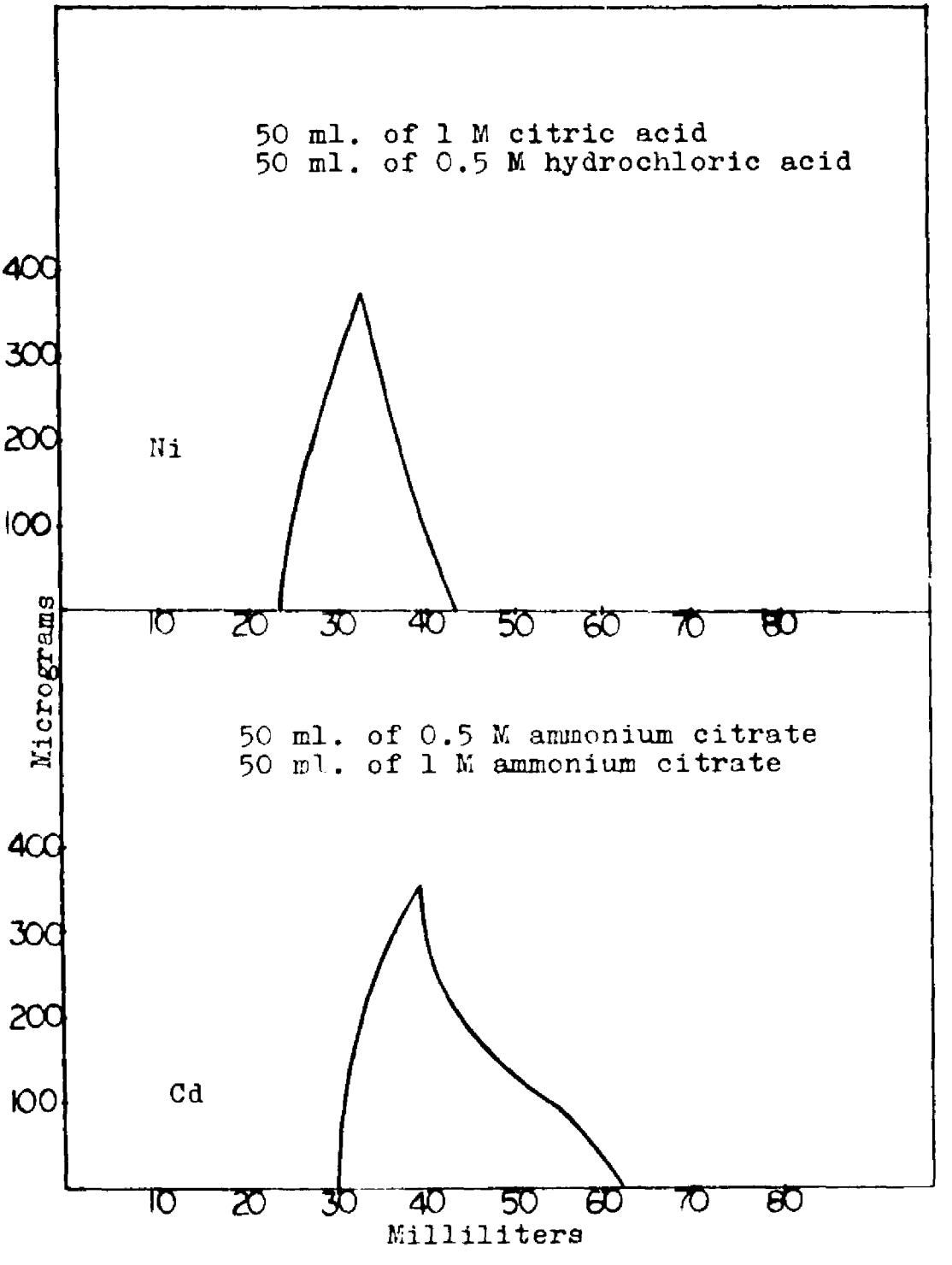

FIGURE 4

ELUTION CURVES FOR CADMIUM AND NICKEL

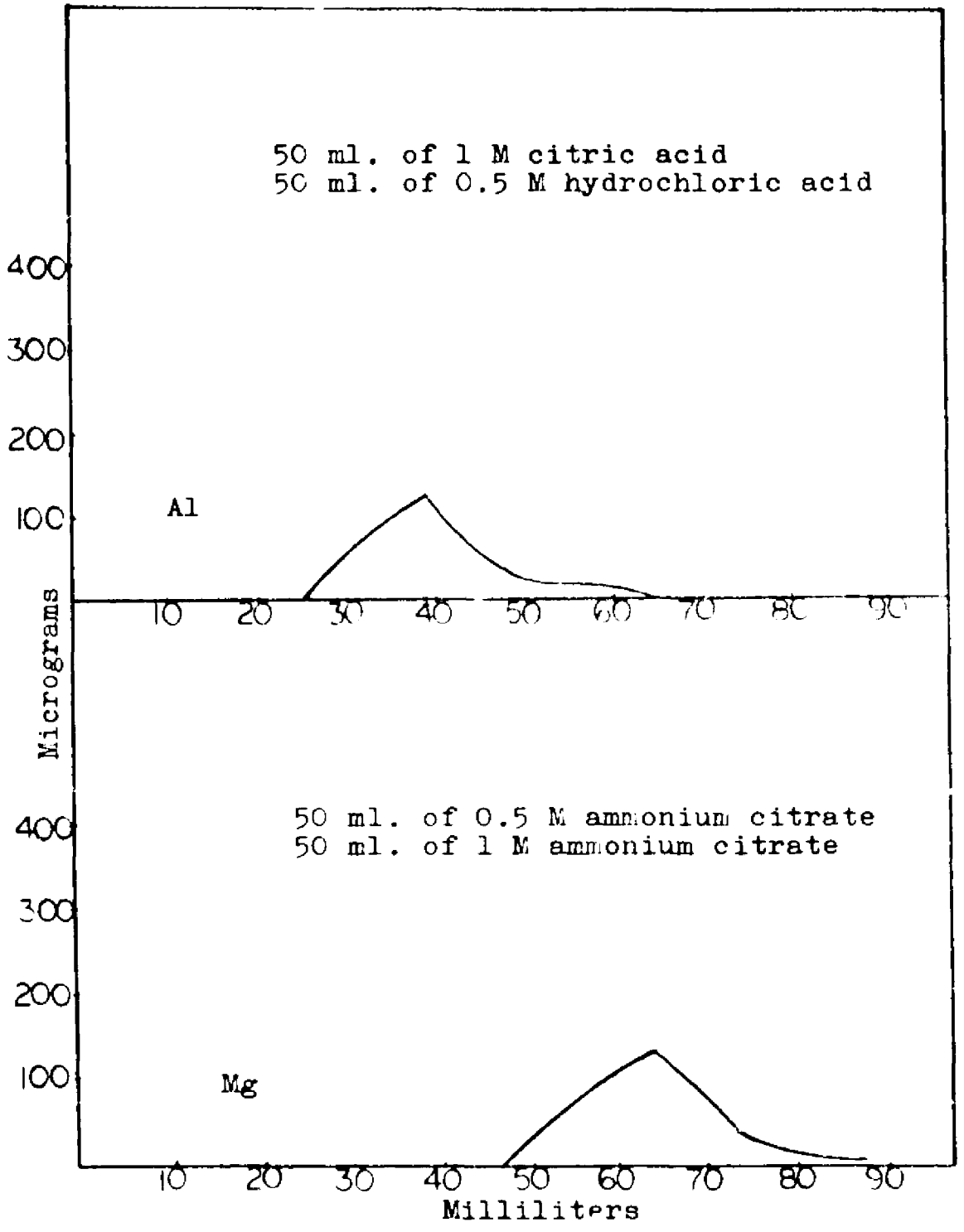

FIGURE 5

ELUTION CURVES FOR ALUMINUM AND MAGNESIUM

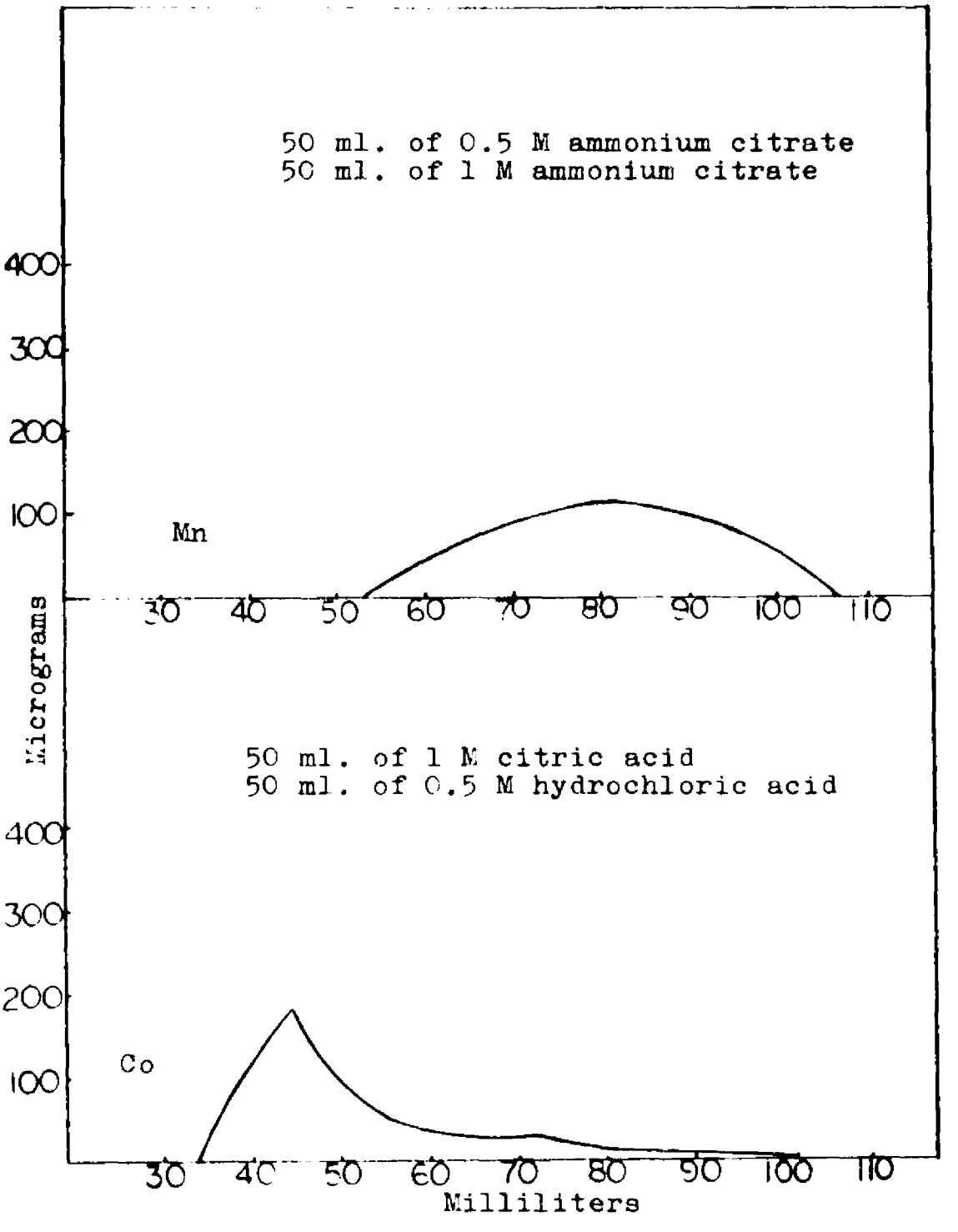

FIGURE 6

ELUTION CURVES FOR COBALT AND MANGANESE

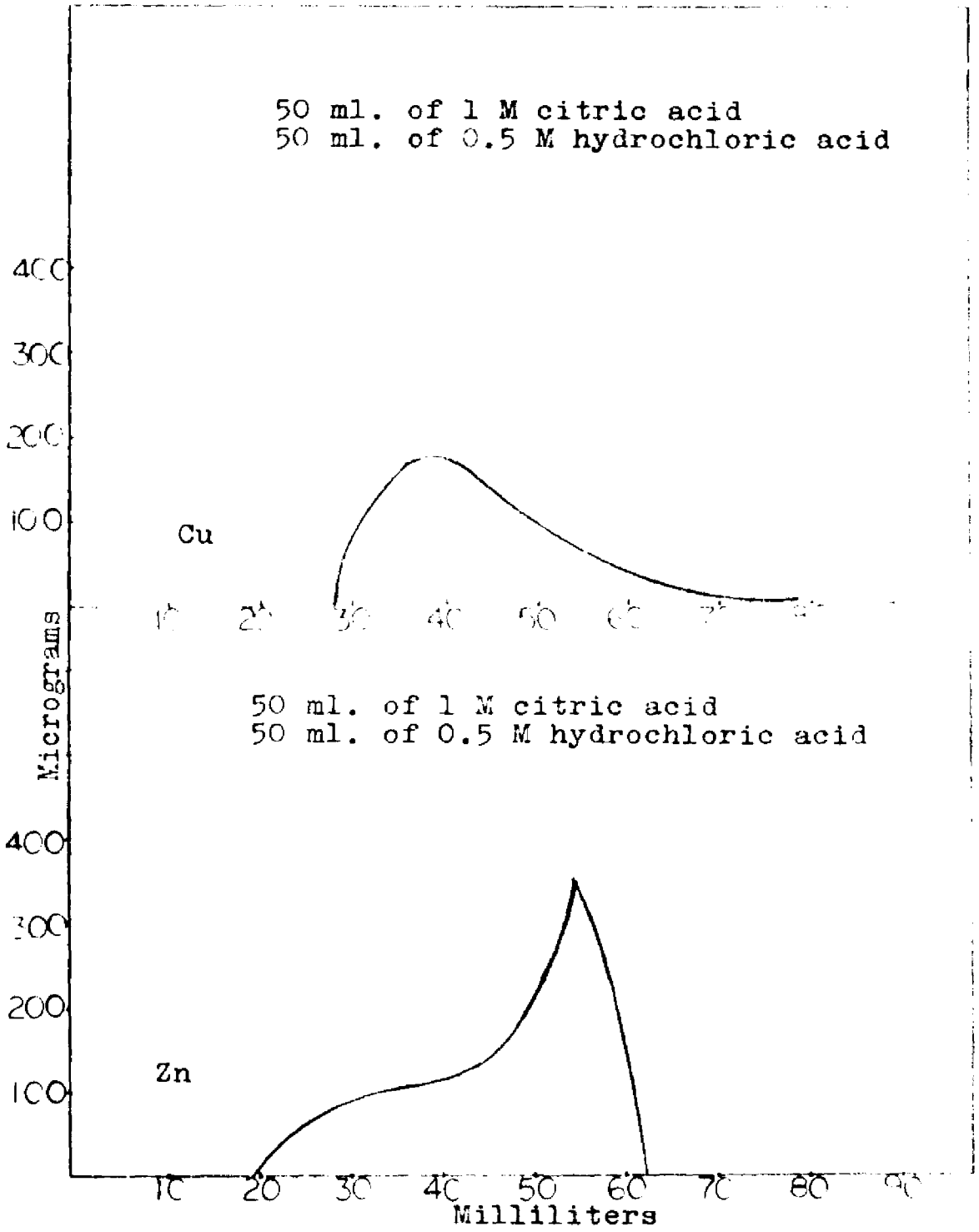

FIGURE 7

ELUTION CURVES FOR COPPER AND ZINC

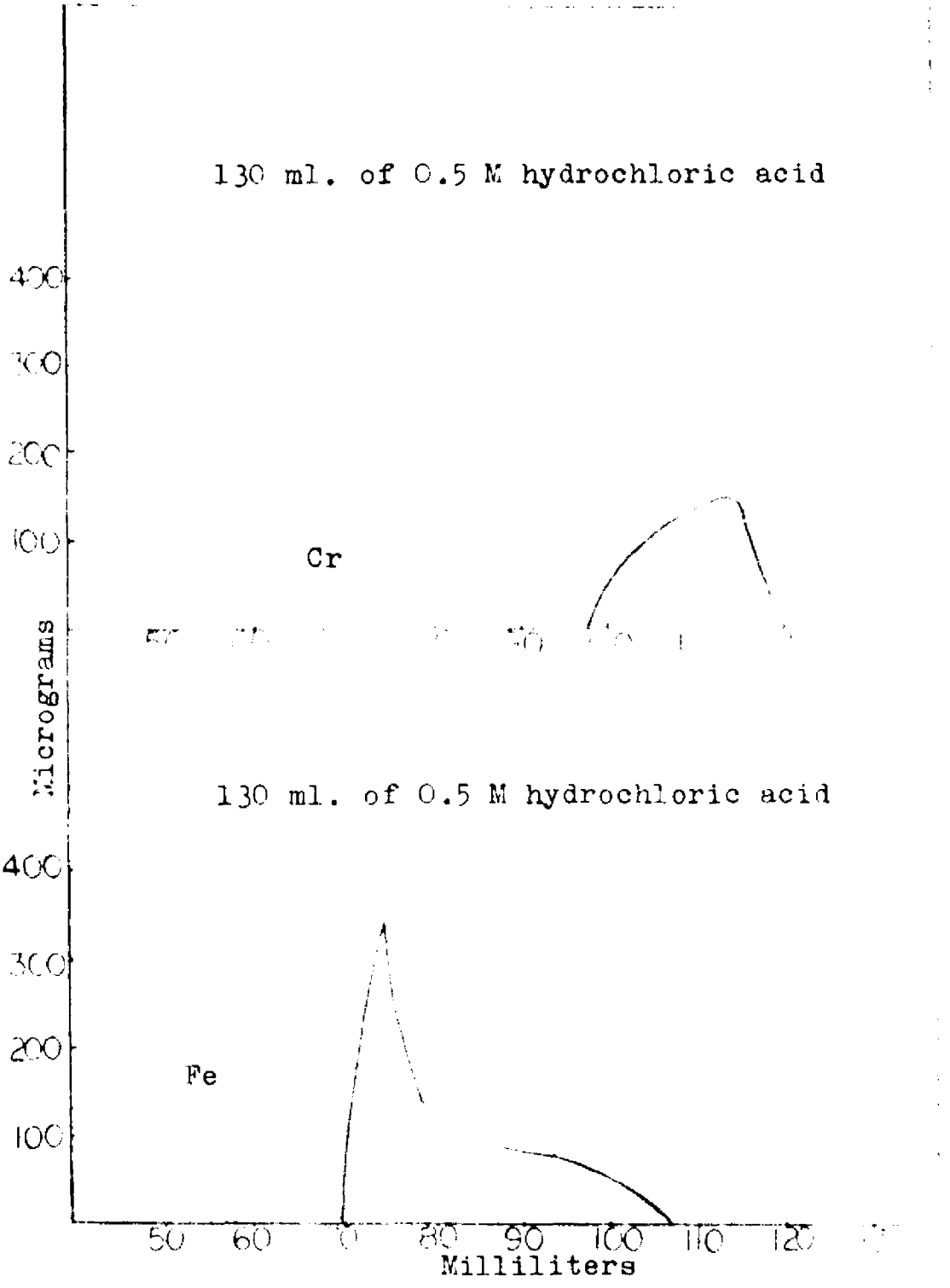

FIGURE 8

ELUTION CURVES FOR CHROMIUM AND IRON

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VITA

Joseph Edward Smith was born November 23, 1923, in Plaquemine, Louisiana. He received his elementary and high school training in the public schools of that city. He entered Louisiana State University in September, 1941. After completing his Freshman year, he entered the U. S. Navy where he served for three years. Upon discharge he reentered Louisiana State University and obtained a B.S. degree in Chemistry in 1948. In the same year he married Valerie Amelia Louapre of New Orleans. He then entered graduate school and obtained a M.S. degree in 1950.

After teaching three years in Paducah Junior College, Paducah, Kentucky and working two years with the state chemist of Indiana at Purdue University, Lafayette, Indiana, he reentered Louisiana State University to begin work on the degree of Doctor of Philosophy.

He has three sons, Alec 8, Marshall 7, and Matthew 1. At present he is Professor of Chemistry and Head of the Department of Physical Science at Arkansas State Teachers College, Conway, Arkansas.

EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: GROUP SEPARATIONS BY ANION-EXCHANGE

Approved:

Maurice La Vache
Major Professor and Chairman

Richard H. Russell
Dean of the Graduate School

EXAMINING COMMITTEE

Philip W. West

J. M. Reynolds

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Date of Examination:

January 10, 1959